Synthesis of Single-Handed Helical Poly(1-dibenzosuberyl methacrylate) *via* Radical Polymerization in the Presence of an Optically Active Cobalt(II) Complex

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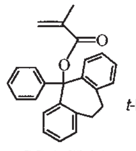
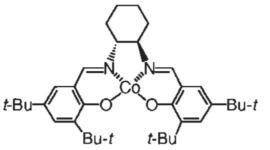
The radical polymerization of 1-phenyldibenzosuberyl methacrylate in the presence of an optically active cobalt(II) complex led to an optically active polymer having a single-handed helical conformation.

Some bulky methacrylates produce highly isotactic, optically active polymers having a single-handed helical conformation through asymmetric polymerization (helix-sense-selective polymerization).[1] The helical polymers show chiral recognition ability toward a wide range of racemic compounds.[2] Although the asymmetric polymerization has been most effectively performed *via* anionic mechanisms,[1] it would be important to develop effective radical polymerization methods leading to facile syntheses of helical polymers having functional groups.[3–5] We recently reported that 1-phenyldibenzosuberyl methacrylate (PDBSMA) produces an optically active, helical polymer by radical polymerization using α,α'-azobisisobutyronitrile (AIBN) in the presence of N,N'-bis(3,5-di-*tert*-butylsalicylidene)-(1*R*,2*R*)-1,2-cyclohexanediaminatocobalt(II)[6] (**1**) although the products were mostly insoluble in solvents and the yield of the soluble, single-handed helical part was low (0.2%).[5] PDBSMA affords a single-handed helical, highly isotactic polymer by asymmetric anionic polymerization[7] and also leads to a nearly perfectly isotactic polymer even by radical polymerization.[8] In the present work, we carried out the radical polymerization of PDBSMA in the presence of N,N'-bis{2-(2,4,6-tri-methylbenzoyl)-3-oxobutylidene}-(1*S*,2*S*)-1,2-diphenylethylenediaminato]cobalt(II)[9] (**2**) and found **2** to be much more effective than **1** in inducing single-handed helicity.



PDBSMA



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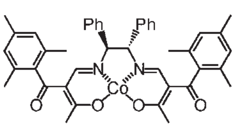

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PDBSMA was prepared according to the literature.[10] **2** (TCI) was used as purchased. The single-handed helical poly(PDBSMA) was available from our previous work.[7] The other experimental details are the same as those in refs. 4 and 5.

The results of the polymerization using AIBN in the presence of **2** in $CHCl_3$-pyridine or in pure $CHCl_3$ are summarized in Table 1. The polymers obtained in this work were nearly completely isotactic (mm > 99%) as found by the ^1H NMR analysis of the PMMA derived from the original products and were partially insoluble in tetrahydrofuran (THF). All the polymerization in the presence of **2** led to an optically active polymer. The circular dichroism (CD) spectrum of the THF-soluble, dextrorotatory polymer obtained in run 2 is shown with that of the single-handed helical polymer obtained by asymmetric anionic polymerization[7] ($[\alpha]_{365}$ + 1780°) in Figure 1. The two spectra have a very similar spectral pattern and differ only in intensity; the CD intensity ratio correspondeds to the ratio of the specific rotation of the two polymers. The other polymers also had similar spectral patterns. These results confirm that **2** induced a helical conformation with excess screw sense.

Table 1. Radical polymerization of PDBSMA with AIBN in the presence of **1** and **2** in a $CHCl_3$-pyridine mixture or in $CHCl_3$[a]

Run	Additive (conc./M)	Temp. °C	MeOH-insoluble part Yield %	DP[b]	Mw/Mn[b]	THF-sol. part[c] Yield %	$[\alpha]_{365}^{25}$ deg
1	**2** (0.055)	60	24	41	1.70	8[e]	+1379[e]
2	**2** (0.035)	60	42	67[d]	1.52[d]	25[e]	+1194[e]
3	**2** (0.015)	60	62	72	2.07	10[e]	+968[e]
4	none	60	75	130	3.01	4[e]	—
5[f]	**2** (0.055)	60	23	126	1.14	9[e]	−553[e]
6[f]	none	60	74	155	3.27	5[e]	—
7[g]	**2** (0.035)	30	37	55	1.82	5[e]	+616[e]
8[g]	none	30	87	132	2.88	—	—
9[g]	**2** (0.035)	0	9	121	1.74	2	−100
10[g]	none	0	76	83	2.29	—	—
11[h]	**1** (0.039)	60	39	78	1.60	3	+550

[a]Conditions: monomer 0.3 g (runs 1, 3, 5, 7), 0.5 g (runs 2, 4, 6, 8–11); $[\text{pyridine}]_o = 0.46$ M (runs 1–4, 7–10), 0.50 M (run 11); time = 24 h (runs 1–6, 11), 48 h (runs 7–10); $[\text{PDBSMA}]_o = 0.44$ M; $[\text{AIBN}]_o = 0.029$ M. [b]Determined by SEC of PMMA derived from the original polymer using standard polystyrenes. [c]Measured in THF (conc. 0.005–0.2 g.dl, cell length 0.5 dm). [d]THF-insoluble part. [e]Washed with a benzene/hexane (3/2, v/v) mixture to remove oligomeric impurities. [f]Reactions in $CHCl_3$. [g]Under UV irradiation using a high-pressure Hg lamp. [g]Cited from Ref. 5.

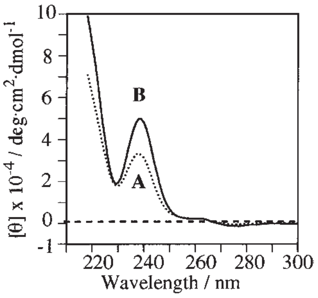

Figure 1. CD spectra of poly(PDBSMA)s obtained by radical polymerization using **2** at 60 °C (run 2 in Table 2; THF-soluble polymer) (A) and by anionic polymerization at −78 °C (THF, r.t.) (B).

The reaction conditions remarkably affected polymerization behavior. The polymer yield and the degree of polymerization decreased in the presence of **2**. In contrast to the fact that no polymer was obtained in the absence of pyridine with **1** as an additive,[5] a polymer was produced in pure $CHCl_3$ using **2** (run 5). In the polymerization at 60 °C in $CHCl_3$-pyridine, dextrorotatory polymers were obtained where a higher concentration of **2** resulted in higher optical activity (runs 1–3). The specific rotation observed in run 1, $[\alpha]_{365} + 1379°$, corresponds to 78% excess of helical sense. Unlike the polymerization in $CHCl_3$-pyridine, that in $CHCl_3$ afforded a levorotatory polymer at 60 °C (runs 1 and 5), suggesting that a **2**-pyridine interaction has a role in the helix-sense selection. In the polymerization in $CHCl_3$-pyridine at 30 °C, the optical activity of the polymer was much smaller than that of the polymer obtained at 60 °C at similar concentrations of the reagents (runs 7 and 2). Moreover, in $CHCl_3$-pyridine at 0 °C, the sign of the optical activity of the product was negative (run 9). An interaction of **2** with solvent and/or monomer or conformational variations of **2** depending on temperature could cause this.

As shown in Figure 2A, the optical activity of the polymer obtained in run 2 was dependent on molecular weight especially in the range below ca. 10^4, while dependence was not so obvious for the single-handed helical polymer synthesized by anionic polymerization[10] (Figure 2B). A quantitative analysis of the intensity ratio of the polarimetric and UV chromatograms, a quantity roughly proportional to specific rotation, indicated that the ratio for the polymer of run 2 was almost constant and comparable to the ratio for the single-handed helical polymer in the molecular weight range over ca. 6×10^3, meaning that the radically obtained products in this range are single-handed helical. The content of the fractions was ca. 72% from the UV chromatographic area in Figure 2A (shaded area), giving the total yield of 18% for the THF-soluble, single-handed helix, taking the yield of the whole THF-soluble polymer into account. In addition, it is noteworthy that in Figure 2A the SEC peaks were present in the molecular weight range up to 10^6, probably due to aggregates. Such high-molecular weight fractions have not been observed for anionically synthesized single-handed helical polymers because of the poor solubility.[7]

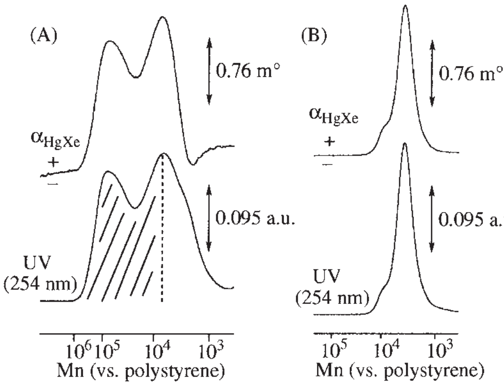

Figure 2. SEC curves of poly(PDBSMA)s measured using a polarimetric (top) and UV (bottom) detectors: the polymer obtained by radical polymerization using **2** at 60 °C (run 2 in Table 2; THF-soluble, benzene-hexane-insoluble part) (A) and that synthesized by anionic polymerization at −78 °C (B). The chromatograms were obtained with a Shodex UV-41 detector (cell length 10 mm) and a JASCO OR990 polarimetric detector (cell length 25 mm) using Shodex KF-803 and KF-806F GPC

In conclusion, the radical polymerization in the presence of **2** effectively produced a single-handed helical poly(PDBSMA). Although the reaction mechanism is still not clear, some Co(II) complexes have been known to interact with growing species in radical polymerization systems.[11,12] Further studies are under way to obtain information of the reaction mechanism and to apply **1**, **2**, and their analogues to radical polymerization of various types of monomers.

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